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Graham,
Robert Orlando
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Concerning certain
Diazo Decomposition Reactions.

Dissertation

presented for the degree of

Doctor of Philosophy

at the

Johns Hopkins University

by

R. O. Graham.

1888.

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Introduction.

A series of investigations for the purpose of discovering, if possible, the [illegible] [illegible] [illegible] [illegible] [illegible] to each of the two decomposition reactions of diazo compounds with alcohol is being carried on in this laboratory under the supervision of Professor [illegible]. This series was begun by Mr. W. R. Orndorff,* who studied the action of [illegible] [illegible] [illegible] diazo benzene nitrate and sulphate, and of the ortho, meta, and para diazo toluene sulphates. I have continued this work by studying the decompositions by alcohol of the para and ortho diazo nitro benzene [illegible] [illegible] [illegible] [illegible] and sulphates; of the para and ortho diazo-benzoic acid nitrates; of meta diazo benzoic-acid sulphate; and of meta diazo para-brom toluene nitrate.

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* Am. Chem. Journal [illegible] 387

I have studied, likewise, the decompositions by water and in toluene of the various diazo nitro benzenes and of para-diazo benzoic acid nitrate; also the decomposition in toluene of ortho diazo benzoic acid nitrate, and of meta diazo benzoic acid sulphate.

II. The Nitranilines.

A. Para Nitraniline. $C_6H_4\begin{smallmatrix}NO_2 (1)\\NH_2 (4)\end{smallmatrix}$.

Preparation of para diazo nitrobenzene nitrate.

Considerable difficulty was experienced in finding the best method for preparing the diazo, especially was the diazo amido compound formed instead. The following was adopted as the most [illegible] delay, and reducing the bulk [illegible], etc.

Twenty grams of the para nitraniline was placed in a ten ounce flask of 150 c.c. capacity, [illegible]

Gradually heating, the para nitraniline was changed to the nitrate, $C_6H_4\overset{NO_2}{NH_2}, HNO_3$. The flask was placed in a cooling mixture, and its contents subjected to a rapid current of nitric oxide, prepared by treating nitric acid on arsenic trioxide. The greatest care was necessary to prevent the formation of the above mentioned amido compound. The flask was removed from the cooling mixture when precipitation began, and was replaced almost at once to prevent too great a rise of temperature. Evidently the proper temperatures for the formation of this chain are included within narrow limits:- probably between 25° and 30°.

[illegible] end of the reaction was signalized by a

change of color in the solution to a dingy green, and by the escape of nitric fumes. After cooling in a freezing mixture of ice and hydrochloric acid, the liquid was filtered quickly into a 400 C.C. flask by aid of the pump, to free from a small quantity of residue that had formed therein. To the thoroughly cooled liquid were added about 250 C.C. absolute alcohol, and 1500 C.C. anhydrous ether, and the flask was constantly agitated in the freezing mixture. In a few minutes, the needle-shaped crystals of the diazo compound separated out. After settling, the crystals were thrown upon a filter, the liquid quickly drained off, and the crystals washed on the filter, first with absolute alcohol, then with anhydrous ether, and spread upon drying paper. From the 20 g. of paranitraniline taken, 16 g. of the diazo nitrate $C_6H_4\begin{smallmatrix}NO_2\\ N-N\,NO_3\end{smallmatrix}$, were obtained.

Description of para-diazo-nitro-benzene nitrate.

The long, needle like crystals have a brilliant, silky lustre, and when first formed are white, but soon become yellow if exposed to the air. The compound explodes violently when heated or struck. It is readily soluble in water; almost insoluble in alcohol and ether.

Decomposition of para diazo nitro benzene nitrate by Alcohol.

Forty grams of the diazo were decomposed in ten-gram lots by placing in a carefully dried flask, covering with absolute alcohol, and connecting the flask with an inverted condenser. After placing upon the water bath, raising the temperature of the bath to 70°, decomposition began; and at 75° went rapidly forward to completion, evolving a strong odor of aldehyde. The various alcohol solutions were collected in a two litre balloon flask,

and the excess of alcohol distilled off. Then freeing the product nearly of water, and adding sodic hydroxide, a current of steam was passed. A liquid volatile in steam passed over, and collected under the water in the receiver. In the flask was left a lumpy mass; apparently the result of a breaking down of some of the decomposition products.

The contents of the flask were acidified by sulphuric acid, and again subjected to the steam current: but no further product volatile in steam was found. From the alcoholic distillates, a small quantity of an oil had settled, which on examination proved to be identical with that carried over by the steam, and it was added to the latter.

Examination of the product volatile in Steam.

[illegible] and nitrogen were given off; and the oil carried over by the water

-vapor, which was the main product of the reaction, had the peculiar bitter-almond odor and other properties of mono nitro benzene, $C_6H_5NO_2$. After separating from water, by use of a separating funnel, and drying over Calcium Chloride, the oil was found to boil at 206°-207°. From 400 g of the diazo, 160 g of mono nitro benzene was obtained; -70% of the theoretical yield.

Attempts were made to extract a crystallized compound from the tarry mass, by use of benzene, Ether and Carbon bisulphide: but these attempts were fruitless.

The following formula represents, eventually, the reaction:- $C_6H_4-\overset{NO_2}{N}=N\,NO_3+C_2H_5OH=C_6H_5NO_2+C_2H_4O+N_2+HNO_3$.

Decomposing para diazo-nitro-benzene nitrate by water.

Twelve grams of the diazo were placed in a 250 c.c. flask half filled with distilled water

and having connected an vertical inverted condenser, it was placed in the water bath. Carefully heating the bath, and all the while keeping the flask in constant agitation, decomposition began around 15°, and at 20° went rapidly forward. Nitrogen was given off and a tarry mass remained in the flask. As the principal product of decomposition, from which a crystallized substance could not be obtained, by means of benzene or ether. A small quantity of light-brown precipitate settled from the water; but here as in all attempts to crystallize was in vain. Evidently the decomposition had resulted in an almost complete breaking down into a tarry mass.

Decomposition of para diazo nitrobenzene nitrate in toluene.

Placing 8 g. of the carefully dried diazo in a dry 200 c.c. flask, about

100 C.C. anhydrous toluene was [illegible] upon this, the flask connected with [illegible] a water bath. Constantly shaking the flask, the temperature was raised to about 110° [illegible] allowed to go on more slowly, to prevent, as far as possible, the breaking down to tar. [illegible] was turning; the toluene colored red; and, in spite of all precautions to keep it low, tar formed, which clung to the sides of the flask. Shaking out the contents of the flask with sodium carbonate, the liquid was poured off in a funnel to separate from toluene. After boiling to perfectly free from traces of toluene, the solution was acidified by hydrochloric acid. A light brown precipitate was thrown down in small quantity, which dissolved in hot alcohol and in ether; but from which I failed to obtain

a crystallized compound. Caustic Soda dissolved it, giving a red color; remains undissolving an amount.

The brown mass, a deep black, semi crystalline solid, resulting from the decomposition, dissolved readily in alcohol; but could not be induced to crystallize.

Attempts to make para diazo nitro benzene Sulphate.

Various methods for diazo formation were tried, in order to obtain the para-diazo Sulphate; but these were unsuccessful. The [illegible], ~~matter~~, and the difficulty occasioned by the ready formation of the amido compound above mentioned, seemed to be the obstacles in the way of obtaining this. Lack of material for further attention, has to be left to [illegible].

B. Meta Nitrodiazobenzene. C_6H_4 [illegible]

Preparation of meta diazo-nitrobenzene nitrate.

Ten grams of meta nitraniline are thoroughly mixed with sixteen grams of strong and a little dilute nitric acids, thus forming the nitrate, $C_6H_4{-}\overset{NO_2}{NH_2}\cdot HNO_3$. Suspending this in about 100 c.c. absolute alcohol, [illegible] ice water, [illegible] concentrated nitric acid [illegible]. The diazo precipitated out as formed. Constant agitation was necessary to ensure the exposure of all the nitrate to the action of the nitrous acid. At the close of reaction, a little ether was added to completely precipitate the diazo from the alcohol; a [illegible] [illegible] the contents [illegible] filter, and [illegible]

speedily as possible with the aid of the filter pump. The solid was washed on the filter with absolute alcohol and then with ether, and dried between drying paper. The compound, meta nitroben-[illegible] of the diazo, $C_6H_4\overset{NO_2\,(1)}{-N=N-NO_3}(3)$.

A second specimen of the diazo was obtained by placing 9.6 g of meta nitraniline in a flask, adding strong nitric acid, and then very gently stirring it. [illegible] 75 c.c. alcohol with [illegible] of water had been added. On treating as before, the diazo was obtained in solution in the water. Filtering by means of a pump, the solution was placed in a freezing mixture, and hydrochloric acid and alcohol and ether added. On agitating the contents of the flask in a freezing mixture, the diazo crystals separated out. [illegible] of the diazo were obtained.

Decomposition of Meta diazo nitro benzene nitrate. This diazo crystallizes

in small grains, which are almost white at first, but which soon become slightly brown on exposure to the air. It is impossible to evaluate [illegible] state than the para-diazo and changes [illegible] When struck, or heated, it explodes; but not so readily as the para compound.

Making of Meta diazo nitro benzene sulfonate.

After repeated experiments, the following method was adopted as best. Ten grams of meta-nitranilin were placed in a flask, and a slight excess of concentrated sulphuric acid added; then [illegible] water. After standing for some time, [illegible] sulphonation had been completed, the flask was half filled with ordinary alcohol, cooled, placed in ice, and nitrous fumes passed in, until these ceased to be absorbed. The brown contents of the flask were then poured quickly upon

a filter, and to the slight quantity of residue in the flask was added the least requisite amount of water, to dissolve out any of the diazo that might be there. The solution thus obtained was filtered, and added to the main body. Placing the flask containing the crystallization in a freezing mixture, on adding ether the granular diazo crystals were speedily precipitated. From 10 g. meta nitraniline, 11½ g. of the sulphate diazo, $C_6H_4\overset{NO_2}{-}N=N-HSO_4$ were obtained.

Description of meta-diazo-nitro-benzene Sulphate.

The crystals of this benzene diazo are perfectly white, granular, and readily soluble in water. Standing over night in a desiccator over sulphuric acid, they have acquired a delicate [illegible] most stable of the nitro benzene diazo compounds, excepting the corresponding ortho [illegible]

days without suffering decomposition to any marked extent. Concussion failed to explode it; and, when exposed to flame, it deflagrated, swelling up, with a black residue.

Decomposition of meta diazo nitrobenzene nitrate by alcohol.

Forty-six grams of this compound, [illegible] covered with absolute alcohol, and the flask [illegible] placed upon the water bath. When the bath reached 70°, decomposition began; and at 75°, went rapidly forward to completion. Aldehyde was given off freely; and a reddish liquid resulted. After the reaction had ceased, the excess of alcohol was distilled off. Treating the residue as in the [illegible] preparation, found, [illegible]

the water-vapor. Acidifying in the contents of the flask, a deposit [illegible] of a white vapor, no [illegible] volatile in steam was formed. Filtering of the liquid, [illegible] a brown mass that had formed in the flask, a decomposition of the smallest bulk, failed to secure any further decomposition products. Nor could a crystallized compound be obtained from the tar.

Decomposition of meta-chloro-nitro-benzene [illegible] by Alcohol.

[illegible] of this was decomposed as in the case of the nitrate. Decomposition began at 65°, and at 70° went rapidly forward. The odor of aldehyde, during the reaction, was stronger than in the nitrate; but on the distilling off the excess of alcohol, the odor was pronounced. The steam current carried over more [illegible], as in the former case; and in

further definite decomposition products been obtained.

Products of the decompositions of the meta diazo-nitro-benzene nitrate and sulphate by Alcohol.

The [illegible]

similar to the corresponding para reaction: and the decomposition products obtained were Aldehyde and mono nitro-benzene, as in the latter case. The mono nitro benzene was the main product in each case. From 46 g. of the meta-diazo nitrate, 15 g. of this were obtained, 55% of the theoretical yield: and from the sulphate, 22 g., there was obtained 7 g. of the mono nitro-benzene, about 66% of the theoretical yield.

The reactions may be represented, respectively, by the following Equations:

$$\overset{NO_2}{C_6H_4}-N=N-NO_3+C_2H_5OH=C_6H_5NO_2+C_2H_4O+N_2+HNO_3.$$

$$\overset{NO_2}{C_6H_4}\,N=N-HSO_4+C_2H_5OH=C_6H_5NO_2+C_2H_4O+N_2+H_2SO_4.$$

Decomposition of meta diazo-nitrobenzene nitrate by heat.

Eight grams of this were decomposed as in the case of the analogous para compound. At 83°, decomposition began; and at 90° went steadily forward. Nitrogen was given off; and, in spite of the precautions taken, tar was the only solid matter resulting, except a small portion of reddish brown precipitate. Neither this precipitate nor the tar could be induced to yield a crystallized compound. The tar was the main product of decomposition.

Decomposition of meta diazo-nitrobenzene sulphate by heat.

Heating 10 g. as in the case of the nitrate, at 85° action began; and continued to go forward slowly at a slightly higher temperature. Nitrogen escaped; and a tarry mass resulted. After the action was

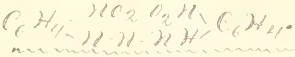
over, ~~[illegible]~~ yielding a yellow tar, the filtrate was set aside. After a time, a yellow, moss like precipitate came out; which, on being slightly heated, tended to change to a [illegible] be crystallized from alcohol; while from ether, indefinitely shaped crystals were deposited on the sides of the vessel, which, on gently heating, broke down into a tar.

Decompositions in toluene of meta-diazo-nitro-benzene nitrate and sulphate.

Twenty-gram quantities of each of these diazo compounds were decomposed as in the case of the para compound. Decomposition [illegible] means employed for the examination of the products, were the same as those already [illegible]

the nitrogen, no definite decomposition-product resulted.

Preparation of the p. [illegible] amido nitro benzene.



$$C_6H_4{-}\overset{NO_2}{N}{-}N{-}\overset{O_2N}{NH}{-}C_6H_4.$$

As has been mentioned previously, great care was necessary to prevent the formation of the diazo-amido, instead of the diazo compound, in the case of para nitraniline. [illegible] the formation of this compound showed itself in the meta nitraniline reaction; but in a less degree. On examination, the para diazo amido-nitro benzene showed it to possess the properties ascribed to this compound by Griess[1], and melted at 226°: the melting point given by Griess being 224.5°. The corresponding meta compound, which Griess found[2] to melt at 195.5°, gave a melting point of 19[illegible]°.

A. Ortho-Nitraniline, $C_6H_4{<}^{NO_2\,(2)}_{NH_2\,(1)}$.

Method of Preparation.

Acetanilide, $C_6H_5NHC_2H_3O$, was prepared according to the method described by W. G. Williams,(1) by heating together aniline [illegible] [illegible] [illegible] [illegible] [illegible] in a flask on a sandbath, and fitted with a cork perforated by condensing tube. An excellent [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] nitro-acetanilide, $C_6H_4{<}^{NHC_2H_3O}_{NO_2}$, by Körner's method.(2) Körner advises that the acid employed be free from the lower oxides of nitrogen. But, having [illegible] prepared an acid of 1.465 Sp. Gr. [illegible] [illegible] [illegible]; and another, having the same specific gravity, by putting together the required proportions of [illegible] [illegible] [illegible] [illegible],

---

(1) [illegible]

(2) [illegible]

it was found that the action of the latter [illegible] was much the more satisfactory.

The introduction of the nitro group was accomplished as follows: In shallow pans, filled with powdered ice, several No. 4 beakers were placed; and in each beaker was poured twenty grams of the acid; and upon this acid was thrown ten grams of the powdered acetanilide. After a few moments, a violent action ensued; and when this was over, the contents of the beaker were emptied quickly into a large evaporating dish containing lumps of ice. After all the acetanilide had been converted into the nitro compound, the latter was filtered from the ice-water, and plunged into an excess of strong caustic potash solution, for the purpose of removing the acetyl group. A mixture of para and ortho nitranilines resulted, together with a charred product of the violent nitration. By distilling in steam for several days, the

volatile ortho nitraniline was carried over by the water vapor. About 120 g. of acetanilide yielded 115 g. of ortho nitraniline. Heating the non volatile portion with very dilute caustic, filtering, and boiling with bone black, the para nitraniline also was obtained.

Preparation of ortho nitraniline nitrate. $C_6H_4{<}^{NO_2\,(1)}_{NH_2 \cdot HNO_3\,(2)}$.

Placing 10 g. of ortho nitraniline in a flask, 45 c.c. dilute, and a few c.c. strong, nitric acids were added thereto, and heat applied; the rising of the nitrate $C_6H_4{<}^{NO_2}_{NH_2} \cdot HNO_3$. Placing the flask in ice water, a rapid current of nitrogen trioxide was passed through the liquid until the completion of the reaction was indicated by the great evolution of nitric fumes. The contents of the flask were filtered by suction pump, and the filtrate placed in a freezing mixture.

In the freezing mixture was placed, also,

two flasks, the one containing 75 c.c. absolute alcohol, and the other 20 c.c. anhydrous ether. Both were [illegible] cooled, and the liquid containing the diazo was poured into the ether and shaken [illegible]. The new diazo solution settled in a layer at the bottom. Adding the cooled alcohol, and agitating for some time in the freezing mixture, the diazo crystallized out. Throwing this upon a filter and quickly drawing off the liquid, the diazo [illegible] dried upon drying paper. Five grams of the nitraniline yielded 9 g. the diazo.

The first attempt to [illegible] this diazo, by placing the liquid containing it in a freezing mixture and adding [illegible], resulted in failure. The active decomposition began at once, which ended [illegible], throwing off [illegible] nitrous fumes; [illegible]

[illegible] in dilute sulfuric acid.

[illegible]

The combination [illegible], form tan crystals, which when dry are much lighter in color, and almost immediately change to a yellow color. These crystals explode on heating, but not by concussion. They are readily soluble in water.

Preparation and description of ortho diazo-nitro benzene sulphate, $C_6H_4\begin{smallmatrix}-NO_2 & (1)\\ -N{:}N\,HSO_4 & (2)\end{smallmatrix}$.

The preparation [illegible] analogous to that already described for the nitrate. From 10g. of ortho nitraniline, 11g. of the diazo resulted. This is a [illegible], crystallizing in small plates. Concussion failed to explode it, and heating [illegible] produced [illegible]. [illegible]

mention frothing up, curling and charring the charred mass, previously spoken [illegible]

Decomposition of ortho diazo nitro [illegible] of the decomposition.

Twenty two grams of this diazo were decomposed in the manner described in the cases of the para and meta compounds. Decomposition began at 70°, and went steadily and rapidly forward to completion. A strong odor of aldehyde was given off. The decomposition was a very clean one, resulting in the formation of but little tarry residue. Distilling in steam, 6 g. of [illegible] were passed over, 54% of the theoretical yield. In the flask remained a small quantity of a brown semi-crystalline solid, which could not be crystallized; and on further decomposition-

product was obtained. Evidently the reaction had taken place mainly according to the following formula.

$$C_6H_4\overset{NO_2}{-}N=N\,HSO_4 + C_2H_5OH = C_6H_5NO_2 + C_2H_4O + N_2 + H_2SO_4.$$

Decomposition of ortho-diazo-nitro-benzene sulphate by water.

Ten grams of the salt were decomposed by water, at 70°, in the manner already described for the analogous para- and meta reactions. A tarry mass was the main product of the decomposition; the residue containing only a brown, amorphous [illegible], from which a crystallized compound could not be obtained.

Decomposition of ortho-diazo-nitro-benzene sulphate in alcohol

[illegible]

[illegible] of the dried diazo compound,

this was placed under 12.5 c.c. anhydrous alco-hol, and heated to the boiling point of toluene without any decomposition. Place [illegible] taken a sand bath and [illegible] [illegible]

[illegible] d, gas was liberated, showed no signs of decom-position. Suddenly the entire quantity decomposed at once, causing a vigorous explo-sion, and leaving [illegible] a tarry mass as remaining decomposition product.

Summing up of the reactions of the diazo compounds [illegible]

The decompositions of the nitrates and sulphates of [illegible] the nitroanilines by alcohol take place, respect-ively according to the following equations:-

$$C_6H_4\overset{NO_2}{-N=N-NO_3} + C_2H_5OH = C_6H_5NO_2 + C_2H_4O + N_2 + HNO_3.$$

$$C_6H_4\overset{NO_2}{N=N-HSO_4} + C_2H_5OH = C_6H_5NO_2 + C_2H_4O + N_2 + H_2SO_4.$$

In each case, the principal product of [illegible] yield of this varying, in different experiments, from 54% to 70% of the theoretical yield calculated per the above formulae.

In every case, the decomposition was attended by a marked odor of aldehyde.

None of the decompositions by alcohol yielded any definite nitrated liquid compound, excepting the mono-nitro-benzene.

The decompositions by water resulted, in all cases, in the production of [illegible] at a [illegible] temperature [illegible] below the boiling point of water, with evolution of nitrogen, and of much tarry mass from which it was possible to obtain crystallized compounds with difficulty.

The decompositions in toluene, in the cases of the para and ortho diazo compounds, took place below the boiling point of water,-

isolate, the ethyl Compound, when the boiling point, delusive, and even explosive violence. In all instances, nitrogen was evolved; and the compounds broke down in a long residue, so that no crystallized substance could be obtained.

III. The Amido-Benzoic Acids.

A. Meta-Amido-Benzoic Acid.

Making of meta diazo-benzoic acid sulphate. $C_6H_4\overset{COOH}{N{=}N{-}HSO_4}$ 13).

This was effected by using the method employed by Griess, who describes this diazo as the [illegible]; but that obtained by me was a beautiful golden tone. It was washed by cold water and dried [illegible] [illegible] compound was obtained.

Decomposition by Alcohol of Meta-diazo-benzoic-acid sulphate.

[illegible]

It was decomposed by [illegible] absolute [illegible]

[illegible]

13) Berichte 9-1655.

the amalgam with conjugate compounds. When the ferment is heated in the bath [illegible] decomposition begins, [illegible] perceived. [illegible], the solution [illegible], [illegible] the evaporation, [illegible] and the [illegible], [illegible] [illegible]. Evaporating the [illegible] alcohol, diluting the residue with water, and distilling in steam, an oil [illegible] with water passed over. Boiling the residual liquid with animal charcoal, filtering, evaporating to [illegible] the volume, and adding hydrochloric acid, no [illegible] crystals was obtained [illegible] only a residue [illegible] [illegible] tar like oil.

Products of the decomposition by Alcohol of Meta-diazo-benzoic acid Sulphate.

[illegible] and [illegible] Scotland.

The oil [illegible] was boiled with the

water; and the water was then shaken up with Ether, in order to obtain the oil suspended therein. Placing the ether extract upon the water bath, the Ether was driven off, and the oil obtained added to the main body.

Drying the oil on Calcium Chloride and distilling, it passed over at 213°. Its boiling point, the pleasant odor, and other properties, showed it to be Ethyl benzoate, $C_6H_5.COOC_2H_5$. Sixty two grams of the diazo gave 24 g. of Ethyl benzoate; about 63 p.c. the theoretical yield, calculated per the formula:

$$C_6H_4\overset{COOH}{-}N{:}N{\cdot}HSO_4{}_{(3)}^{(1)}+C_2H_5OH=C_6H_5COOC_2H_5+N_2+H_2SO_4.$$

Saponifying 5 g. of the oil with Caustic potash, and then acidifying by hydrochloric acid, benzoic acid was precipitated, which, on being recrystallized, melted at 120°.

Fittica[1] describes [illegible] [illegible] ethoxy benzoic acid as the main decomposition product: but this must have been due to some varying conditions.

[1] B[illegible]

Decomposition of meta-diazo-benzoic acid by means of toluene.

Six grams of the [illegible] diazo was placed, under anhydrous toluene, in a flask arranged as has already been described. No evidence of decomposition was apparent, until the bath reached the boiling point of water; then suddenly the body was collected on the surface of the toluene, and a rapid decomposition ensued, evolving nitrogen, and causing the formation of a tar-like residue. From the decomposition products, nearly [illegible]

B. Ortho Amido-Benzoic Acid.

Preparation of ortho-diazo-benzoic acid nitrate. $C_6H_4\overset{COOH\ (1)}{N:N\,NO_3}$ (2).

Ten grams of ortho-amidobenzoic acid was changed to the nitrate, and from this the diazo compound by employing the method described by Griess. Throwing this upon the filter and quickly draining off the liquid, the diazo was washed in absolute alcohol, then in ether, and spread upon drying paper. From 10 g. of acid taken, 10 g. of diazo obtained, which at first was white, but on exposure to the air, soon took on a yellowish tinge. [illegible]

Decomposition of ortho diazo benzoic acid nitrate by alcohol.

Placing 24 g. of this diazo in a flask and covering with absolute alcohol, it was decomposed in the manner previously described. [illegible] rapidly proceed to completion, with the evolution of aldehyde. Evaporating off the excess of alcohol, diluting the residue with water, and distilling in steam, ethyl benzoate was carried over, as in the case of the meta [illegible] treating the [illegible] in the flask in the manner described for the meta decomposition, benzoic acid was found in small quantity. The main reaction was the formation of ethyl benzoate:- twenty four grams of the diazo yielding 8 g. of this oil, - 53 % of the theoretical yield, calculated from the following equation:

$$C_6H_4\begin{matrix}COOH \\ N{=}NNO_3\end{matrix} \begin{matrix}(1) \\ (2)\end{matrix} + C_2H_5OH = C_6H_5COOC_2H_5 + N_2 + HNO_3$$

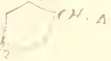
Decomposition of ortho-diazo-benzoic-acid nitrate in toluene.

Eight grams of this were heated in a flask under water with toluene. No signs of decomposition were manifest until the boiling point of water was reached; and at this point the action set in so violently as to necessitate removal from the bath; and for some time after removal decomposition continued vigorously. Meanwhile the flask was constantly shaken; and when the action ceased, was heated carefully again until the decomposition was completed. Then a solution of barium carbonate was added, and the flask thoroughly shaken. The toluene was drawn off by use of a funnel, and tested for substances in solution, but none was found. The solution in barium carbonate, after boiling to free from traces of toluene, and acidi-

[illegible]

from the barium sulphate precipitated.

After a time a precipitate formed which, after being repeatedly boiled with animal charcoal and recrystallized, consisted of long, needle like, yellowish crystals, which melted at 228°, and which in solution gave a blood-red precipitate with ferric chloride. [illegible] ascribed by Griess[1] to unsymmetrical meta nitro salicylic acid.



Each of the materials resulted from decompositions involving the ortho and meta diazo-benzoic acid nitrates.

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[1] Berichte, 11-1730.

The Para Cumic Diazo [illegible] of [illegible]

Making of para-diazo-benzoic acid nitrate. $C_6H_4\overset{COOH\,(1)}{-N\,N\,NO_3}(4)$ A.

The method employed was similar to that described by Griess[1]. Taking 1 g. of the acid and treating with the [illegible] amount of strong nitric acid, this was changed to the nitrate. To this was added sufficient dilute nitric acid to form a thin porridge-like mixture. Then a rapid current of [illegible] generated by nitric oxide was passed until the contents of the flask had become liquid. Rapidly filtering to free from [illegible] a [illegible] mixture, alcohol was added and ether when the diazo-compound crystallized out, [illegible] further [illegible] solidification [illegible].

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[1] Annalen, 120-125.

throwing the contents upon a filter, the liquid was drawn out, The crystals were washed with ether and spread upon drying paper.

[illegible] nitrate.

When thrown down en masse, the compound had much the appearance of light brown sugar. When crystallizing from a more dilute solution, the crystals took the form of fine needles; and from a large excess of alcohol and ether, after several days, thick, colorless, monoclinic prisms, terminated by an ortho [illegible] compound; and was not decomposed by standing, for several days, exposed to the air, nor by concussion, but explodes when heated. It is easily soluble in water: insoluble in absolute alcohol and in ether.

A nitrogen determination of paradiazo-[illegible] nitrate, [illegible] precipita-tion by water, yielded the following result:-

Used [illegible] . [illegible] g.

Calculated for $C_6H_4\overset{COOH}{N=N-NO_3}$.

Found	Theoretical.
N - 11.83 %.	11.60 %.

Decomposition of para diazo benzoic acid nitrate by alcohol.

Twenty-four grams of the diazo [illegible] were decomposed in the manner already [illegible] and at 78° the [illegible], a faint odor of aldehyde was perceptible. Driving off the excess of alcohol, diluting with water and passing steam through, a small quantity of an oil, [illegible] passed into the [illegible]

By acidifying the residual portion in the flask, a solid was precipitated; and it was thrown upon the filter and freed from liquor.

Examination and description of the decomposition products.

The 24 g. of diazo taken yielded about 2 g. of the Ethyl benzoate. The solid thrown down was found to be sublimable; and a portion of it was placed between watch glasses and sublimed through filter paper, thus forming white feather-like crystals. These were found to be acid in character, difficultly soluble in cold water, readily in alcohol. The melting point was found to be 196°. All the properties correspond with those ascribed by Fuchs[1], and by Ladenburg and Fitz[2], to para Ethoxy-benzoic acid, $C_6H_4\begin{smallmatrix}COOH.(1)\\ OC_2H_5.(4)\end{smallmatrix}$. From the 24 g. of diazo taken, between 9 g. and 10 g. of the acid were obtained, — about 50% of the theoretical yield calculated on the formula: $C_6H_4\begin{smallmatrix}COOH\ (1)\\ N=N-NO_3\ (4)\end{smallmatrix} + C_2H_5OH = C_6H_4\begin{smallmatrix}COOH\ (1)\\ OC_2H_5\ (4)\end{smallmatrix} + N_2 + HNO_3$.

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1) Berichte 2-625.
2) Annalen 141-255.

The identity of [illegible] Compound salts [illegible] described by [illegible], and by Ladenburg & Fittig [illegible] [illegible] and examining a number of the salts the many obtained [illegible] were found to agree closely with the corresponding salts described by Ladenburg & Fittig[1].

The Barium Salt, made by adding Barium Chloride to a neutral solution [illegible] of the Ammonium Salt of this acid, formed in [illegible] plates [illegible] white, [illegible] [illegible] which some extent in cold water [illegible] readily [illegible]

[illegible]

The Ammonium Salt is very soluble in water, [illegible] [illegible] saturated solutions. [illegible] crystallizes in small, white, tabular crystals, which tend to gather [illegible]

The Silver Salt, made by adding Silver Nitrate to a neutral solution of the

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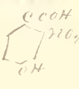
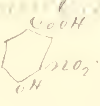
[1] Annalen 141-255

ammonium Salt, at first Canary color [illegible] a brick red, [illegible] ous precipitate, quite Soluble in Cold water, with difficulty Soluble in hot water. When dissolved in hot water and filtering, the Salt Crystallized in [illegible] white needles.

The Lead Salt, made by adding lead acetate to the neutral Ammonium Salt, was thrown down at once as a white, ammoniacal precipitate, much less Soluble in cold water than the barium Salt. In hot water it dissolved readily, and [illegible] needle-like Crystals Came out, hard to distinguish in appearance from those of the barium Salt.

The Calcium Salt, made by adding Calcium Chloride Solution to the neutral Ammonium Salt, formed only slowly, and only in Concentrated Solution. The Salt gave white, needle like Crystals, quite Soluble in water.

Decomposition of para-diazo-benzoic acid nitrate by water.

Eight grams of the diazo-benzoic acid [illegible] the manner described for the corresponding benzene compounds. Beginning at 80°, decomposition went on rapidly, onward to completion at 90°. The contents of the flask were filtered to free from a small amount of brown substance that had formed, then boiled up with animal charcoal, filtered and set aside to crystallize; and this was repeated several times. At last, two well crystallized compounds separated out; the one in considerable quantity as the main product of the reaction, in granular, yellowish crystals melting at 178°, and showing the properties of [illegible][1] [illegible] oxybenzoic acid;  or ;

the other, found in small quantity, formed

[1] Berichte 12. 520.

large, light brown crystals, [illegible] together in radiating arranged groups, melting at 210°, and [illegible] the properties of para oxybenzoic acid. $C_6H_4 \begin{cases} COOH\ (1) \\ OH\ (4) \end{cases}$. Evidently the main reaction took place according with the following formula:-

$$C_6H_4 \begin{cases} COOH\ (1) \\ N{=}N{-}NO_3\ (4) \end{cases} + H_2O = C_6H_3 \begin{cases} COOH\ (1) \\ NO_2\ (2\ or\ 3) \\ OH\ (4) \end{cases} + N_2 + H_2O.$$

According to Griess[1], para oxybenzoic acid should have been the only solid decomposition product; his formula being:

$$C_6H_4 \begin{cases} COOH\ (1) \\ N{=}N{-}NO_3\ (4) \end{cases} + H_2O = C_6H_4 \begin{cases} COOH\ (1) \\ OH\ (4) \end{cases} + N_2 + HNO_3.$$

Decomposition of para diazo benzoic acid nitrate in toluene.

This decomposition was conducted as in the analogous ortho compound. Decomposition was quite apparent at 90°, and, at the boiling point of toluene, went rapidly forward, with evolution of nitrogen. [illegible]

[1] Annalen 120.126.

many [illegible], and the formation of this could not be certainly proved by [illegible]. After the action had ceased, the solution was boiled with a small quantity of water and barium carbonate; and the barium separated, as far as possible. Filtering and allowing to stand, a barium salt was formed, which. This was repeatedly boiled with animal charcoal and filtered. On acidifying with sulphuric acid, and filtering, there formed on standing, a mass of small, light yellow, compact crystals

water and in alcohol, melted at 178°, and showed the properties given by Maybery for the Orthonitro paraoxytoluic acid, $C_6H_3\begin{cases}COOH(1)\\NO_2(2or3)\\OH(4)\end{cases}$ – the same acid that was found as the main product in the water decomposition. The formation is result of the molecular [illegible]; or, rather, a rearrangement of the molecule, i.e.: $C_6H_4\begin{cases}COOH(1)\\N{-}N{-}NO_3\end{cases} = C_6H_3\begin{cases}COOH(1)\\NO_2(2or3)\\OH(4)\end{cases}$,

Summarizing of the diazo compounds [illegible] reactions.

* [illegible]

The ortho and meta diazo compounds gave Ethyl benzoate, $C_6H_5COOC_2H_5$, as the chief decomposition product.

The para diazo compound gave para-ethoxybenzoic acid, $C_6H_4\begin{matrix}COOH(1)\\OC_2H_5(4)\end{matrix}$, as the main product.

In all these cases, a faint odor of aldehyde was apparent.

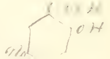
The only secondary definite organic products obtained were small quantities benzoic acid from the ortho compound, and a little ethyl benzoate from the para compound.

The following formulas represent the main reactions with alcohol:

$C_6H_4\begin{matrix}COOH\\N=N-X\end{matrix} + C_2H_5OH = C_6H_5COOC_2H_5 + N_2 + HX$, for ortho and meta

$C_6H_4\begin{matrix}COOH\\N=N-NO_3\end{matrix} + C_2H_5OH = C_6H_4\begin{matrix}COOH(1)\\OC_2H_5(4)\end{matrix} + N_2 + HNO_3$, for the para compound.

III. In the decompositions in toluene.

The ortho diazo compound gave unsymmetrical meta nitro-salicylic acid, 

as the main product of decomposition; the rearrangement of the molecule being represented by the following equation:-

$$C_6H_4{}^{COOH\,(1)}_{N=N-NO_3\,(2)} = C_6H_3{}^{COOH\,(1)}_{OH\,(2)} + N_2.$$

The meta compound yielded no definite solid or liquid decomposition-products.

The para compound gave isometric nitro para oxybenzoic acid, $C_6H_3 \begin{matrix} COOH(1) \\ NO_2(2\ or\ 3) \\ OH(4) \end{matrix}$, as the main decomposition product; the rearrangement being represented by the formula

$$C_6H_4{}^{COOH\,(1)}_{N=N-NO_3(4)} = C_6H_3 \begin{matrix} COOH(1) \\ NO_2(2\ or\ 3) \\ OH(4) \end{matrix} + N_2.$$

These reactions in toluene support the theory in regard to the rearrangement of the molecule advanced by Remsen & Orndorff[1] as every precaution was taken to insure the absence of water.

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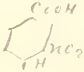
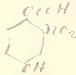
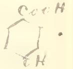
[1] Am. Chem. Journal. 9-396.

VIII. On the decomposition by water.

The para diazo compound gave two well defined crystallized substances; the first one being ortho nitro para oxybenzoic acid, and the other, para oxybenzoic acid: the former being  or  and the latter, .

[illegible]

$$C_6H_4\overset{COOH}{N=N}-NO_3(4) + H_2O = C_6H_3\overset{COOH(1)}{\underset{OH.(4)}{-NO_2(2\ or\ 3)}} + N_2 + H_2O.$$

Lack of material prevented the decomposition by water of the ortho and meta compounds.

Comparison of the reactions obtained by alcohol decomposition with those given by Griess for these compounds.

The general [illegible] given by Griess for the decompositions by alcohol of the [illegible] benzoic acids is.

$$C_nH_{n-7}NO_4 + NO_3 + C_4H_6O_2 = C_nH_{n-8}O_4 + C_2H_4O_2 + 3HO + N_2;$$ or in modern form: $C_6H_4\overset{COOH}{\cdot}NH_2 + C_2H_5NO_2 = C_6H_5-COOH + C_2H_4O + N_2 + H_2O$.

[illegible]

It will be seen that the ortho and meta com-
[illegible] decomposition [illegible] with [illegible]
[illegible]
that a remarkable feature is introduced
into the decomposition. Instead of the alcohol
being permitted to reduce to aldehyde, the
benzoic acid, while in the nascent state,
so to speak, seized upon the ethyl, forming
[illegible]
acid and aldehyde. On the other hand,
the expression for the para-diazo[illegible]
was entirely different from that of
[illegible] as the [illegible] formula [illegible]
product obtained being an ethoxy[illegible]
[illegible].

$$C_6H_4\begin{matrix}COOH\ (1)\\ N=N-NO_3\ (4)\end{matrix} + C_2H_5OH\quad C_6H_4\begin{matrix}COOH\ (1)\\ OC_2H_5\ (4)\end{matrix} + N_2 + HNO_3.$$

A reaction similar to that given by the ortho and meta-diazo compounds here examined, was found by Meyer & Stüber[1] who obtained ethyl benzoate in decomposition by alcohol of the diazo from benzamide, $C_6H_5CONH_2$.

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[1] Annalen 165. 187.

The Alkyl-para oxybenzoic acids.

A glance at the products obtained in the decomposition of alcoholic para diazo-benzoic-acid nitrate reveals the fact that we have here discovered a method which may be advantageously employed in the preparation of the above-named homologous acids.

The methyl para-oxybenzoic acid, $C_6H_4{-}{}^{COOH}_{OCH_3}$, commonly known as anisic acid, had been prepared previously in various ways: by oxidizing anethol, $C_6H_4{-}{}^{OCH_3}_{CH:CH.CH_3}$; of anisol, $C_6H_5{-}OCH_3$; or of the methyl ether of para-cresol, $C_6H_4{-}{}^{OCH_3}_{CH_3}$.

The ethyl para-oxybenzoic acid had been made but twice previously; and in both cases by difficult and laborious processes. Ladenburg and Fitz[2] obtained it in 1867 by heating a mixture of para-oxybenzoic acid, caustic potash and ethyl iodide at 120°, in sealed

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1) Annalen 141-248.
2) [illegible] 141 [illegible]

[illegible], thus forming the ethyl ether of para oxybenzoic acid, $C_6H_4{-}\overset{COOC_2H_5}{OC_2H_5}$; then heating this oil with a hot solution of caustic potash.

In 1869, Fuchs[1] prepared it by boiling potassium cresolate, $C_6H_4{-}\overset{CH_3}{OK}$, with a slight excess of ethyl iodide and a little ethyl alcohol in a flask connected with an inverted condenser; then forming the ethyl ether of cresol, $C_6H_4{-}\overset{CH_3}{OC_2H_5}$. [illegible] with acetic acid and acid chromate of potassium, for several days, in a flask connected with an inverted condenser; and in this way he obtained a small quantity of the acid.

By subjecting para amido benzoic acid to the diazo reaction, then decomposing the diazo compound by alcohol, the yield of para ethoxybenzoic acid is about 4 p.c. of the weight of para-amido benzoic acid taken.

In order to determine whether other alcohols cause an analogous decomposition,

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[1] Berichte 2. 625

this diazo was decomposed by methyl, and also by propyl, alcohols.

Decomposition of para-diazo-benzoic-acid nitrate by methyl alcohol.

Decomposition began at 57°; and at 62°, went vigorously forward, evolving a [illegible] the action, water was added to the alcoholic solution; and the precipitate thus thrown down was washed and recrystallized. The crystals showed all the properties of anisic acid; and a sublimed portion gave a melting point of 185°. From 10 g. of the diazo, about 4 g. of anisic acid resulted.

Decomposition of para-diazo-benzoic-acid nitrate by propyl alcohol.

When the bath was heated to 48°, decomposition began; and this completed

ling at 85°. There was a slight odor of propyl aldehyde. After throwing down the decomposition product and purifying the glucoside as in the case of the analogous methyl compound, it was found that [illegible] grams of the digested yielded about six grams of para propyloxybenzoic acid. $C_6H_4 \begin{smallmatrix} COOH (1) \\ OC_3H_7 (4) \end{smallmatrix}$.

Description of the new acid.

After crystallizing from dilute alcohol; then boiling up with animal charcoal in water with a little alcohol added, and filtering while hot, crystals in the form of shining plates, having generally the appearance of fish-scales, were obtained, which are acid, are insoluble in cold water, with difficulty in hot water, readily soluble in alcohol; and which melt between 141.5° 142.5°. By sublimation, the acid crystallizes in white plates. Evidently the new compound is a homologue of anisic and para-ethoxybenzoic acids.

An analysis resulted as follows:

Substance taken .2442 g.

For formula $C_6H_4{\overset{COOH.}{-}}OC_3H_7$

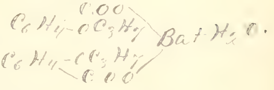
Found.	Estimated.
Carbon {.1634 g.	.1628 g.
[illegible]	[illegible]
Hydrogen [illegible]	[illegible]
{6.590%	6.666%

Salts formed from para-propoxy benzoic acid.

Barium [illegible] By addition of barium chloride to the neutral ammonium salt, was thrown down as a white flocculent precipitate, somewhat soluble in cold water, readily soluble in hot water. From the hot water solution, the crystals separated in microscopic flocculent masses.

On analysing the salt gave the following results;

[illegible]

For formula 

$$\left.\begin{array}{l} C_6H_4{-}OC_3H_7 \\ \quad COO \\ C_6H_4{-}OC_3H_7 \\ \quad COO \end{array}\right\rangle Ba + H_2O.$$

Found. Estimated.

Ba SO4 .0421 g.

Ba. 26.97 % .... 26.70 %.

The Silver Salt was made by adding silver nitrate to the neutral ammonium salt. It appeared in the form of a white, curdy precipitate, insoluble in cold water, and with difficulty in hot water. From the hot water solution, forming small needles. [illegible]

The Lead Salt, made by adding lead acetate to the solution of the ammonium salt, was thrown down as a white, curdy precipitate, almost insoluble in cold water,

readily soluble in hot water and [illegible], [illegible] from the hotter solution in small, radiating [illegible]

[illegible] Salt, formed by adding a solution of Calcium Chloride to the solution of the ammonium salt, a powdery [illegible] precipitate, soluble to some extent in cold water, and more readily in hot water. From solution in hot water, the salt crystallizes in small, [illegible] crystals.

IIIa. Para Diazotoluidine, C_6H_3 [illegible]

Preparation of para-bromtoluidine.

This is accomplished by heating para-bromtoluene with fuming nitric acid; then reducing the nitro compound thus formed by use of tin and hydrochloric acid.

Seemingly the various authorities differ respecting the compounds formed by these reactions, and respecting the properties of these compounds, that a brief summary of their conclusions may prove not uninteresting.

Employing the para-bromtoluene as a starting point, by first introducing the nitro group and then reducing, Körner[1] obtained but one bromtoluidine, melting at 57°.

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1) Zeitschrift für Chemie. 1869-636.

Ostrowski[1] obtained two nitro compounds; one melting at 43°, the other remaining liquid at -20°. By reduction, he obtained from the solid compound a liquid brom-toluidine; and from the liquid nitro compound, a solid brom toluidine, melting at 60°.

Hübner & Roos[2] found two nitro compounds: one melting at 45.5°; the other a liquid. By reduction, the solid brom-nitro toluene gave a para-bromtoluidine melting at 32°; and the liquid nitro compound gave the same brom toluidine, and another, melting at 73°.

Neither of the articles informs us as to the properties of the various products of the reactions, and concerning the products obtained by these reactions, the conversion of para-brom-toluene into brom toluidine was carried forward with all necessary precautions.

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[1] J. für C. 1870-166.

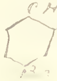
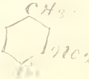
[2] Berichte 6. 799.

Three hundred Grams of a very pure specimen of para brom toluene were changed to the nitro compound in the following manner.

Twenty grams of the para brom toluene were placed in a deep beaker with [illegible] water, and 30 g. of fuming nitric acid gradually added. Vigorous action ensued, accompanied by escape of nitric fumes; the completion of the reaction being marked by a clearing of the solution. The contents of the beaker were then thrown into water; and the heavy oil settled to the bottom. Since the toluene had been converted to the nitro compound in this manner, the oil was thoroughly washed to remove nitric acid, and then separated [illegible]. On standing, a solid crystallized out at the temperature of the room. Placing the [illegible], in a reducing mixture of tin and hydrochloric acid, complete

Solidification resulted. In a [illegible] [illegible] [illegible], the solid then formed was turned out into linen sacks, and placed in an oil press. On application of pressure, a liquid was forced out; and a solid remained in the sack. The latter was crystallized repeatedly from alcohol; and in this manner, the long, needle-like crystals were obtained, which melted sharply at 45.5°.

Next taking the liquid portion which, by consideration, contained some of the solid in solution, it was placed in a [illegible] flask and distilled in steam, in order to obtain as pure a product as possible. It was then separated, and dried by means of [illegible] and [illegible] [illegible], [illegible] Schimmel [illegible] [illegible] to [illegible] at the ordinary temperature, [illegible]. It was placed in the freezing

-ing point, -23°, it solidified; but became liquid again on warming in this. Thus evidently had been formed two distinct brom-nitro toluenes:-  NO_2, and .

Reducing the solid nitro compound, melting-point 45.5°, by use of tin and hydrochloric acid, breaking the double salt formed by caustic potash, and distilling in steam, a para-brom-toluidine passed over with the steam, an oil. This was separated the water, and changed to the nitrate by addition of dilute nitric acid; and this nitrate was purified by recrystallizing by boiling up with animal charcoal in water. [illegible] crystals thus obtained were treated with ammonia, distilling with steam the [illegible] this oil was placed in ice water; and at

and formed a [illegible], yellow solid, which melted at 32°.

Subjecting the liquid para-brom-nitro-toluene to the process just outlined, [illegible] crystallized nitric acid salt by means of ammonia, a liquid resulted which, after being completely dried, slowly solidified when placed in ice-water, and when so remained solid on removal therefrom, but very slowly, and tended to become liquid at a temperature of 25°. Evidently the solid para-brom-toluidine held in its meshes a small amount of liquid para-brom-toluidine.

In driving off the para-brom-toluidines, the distillation in steam had been continued, in each case, until the water collecting in the receiver came over colorless. These distillates were collected, acidified with hydrochloric acid,

Evaporated to small volume, filtered, and the solid allowed to crystallize out. This solid was boiled up with animal charcoal in water containing a little alcohol, and filtered. On cooling, colorless, spear-shaped crystals of the hydrochloric acid salt came out. Treating with ammonia, the base was freed as an oil; and this, on being placed in ice water, formed a solid which remained firm, brittle and dry at the temperature of the room, and melted at 32°, being identical with that obtained from solid para-brom-nitro-toluene. The most careful search had failed to find a trace of the 75° melting compound described by Hübner & Roos.[1]

[illegible] obtained by me correspond with those secured by Hübner & Roos, except that in my work the toluidine resulting from the reduction of the liquid nitro compound was evidently

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1) Berichte 6 799.

a mixture, solid and liquid toluidines, the liquids so obtainable, however, consisted [illegible] and from distilled, 9 g. of para toluidine melting at 32°.

Preparation and decomposition of para from meta-diazo-toluene nitrate by alcohol.

Several attempts were made to obtain the diazo compound; but without success.

Then 48 g. of the nitrate was placed in a flask, and ethyl nitrite, made by saturating absolute alcohol with the nitrous fumes, was added. Placing the flask in a water bath, and connecting with an inverted condenser, when heated to 70° the diazo compound was formed, and decomposed by the alcohol with a sweet odor of aldehyde. After the action had ceased, the excess alcohol

and ethyl nitrate was evaporated off, the residue was then diluted with water, and the steam current passed. The oil, volatile with water vapor, was drawn over, and on cooling, crystals separated out from the residue in the flask.

Examination and description of the decomposition products.

The crystals separating from the residual liquid were in small quantities as compared with the oil drawn over. They were found to be crystals of two different compounds; [illegible] in yellow [illegible] needles; and the other having yellow, granular crystals, which collected on the sides and at the bottom of the vessel. Various attempts made to separate completely these crystals were unsuccessful. From a small portion of [illegible] from the mixture, the other compound, separated [illegible] by

mechanical means, the melting-points, the boiling compound was found to be about 138°-135°. [illegible] 160° 170°. The former contained bromine and nitrogen; the latter, bromine, but probably no nitrogen whatever.

Separating the oil, that had passed over, from the water, and drying over calcium chloride, the [illegible] ether, found as the main product of the decomposition, was distilled repeatedly; but no compound could be obtained therefrom having a definite boiling-point; first beginning to boil at 150°, the mercury steadily rose to 230°. The quantity was too small to allow of separation by fractional distillation; and the compounds evidently had nearly the same specific gravities. The oil contained bromine but gave no test for nitrogen.

Attempt to distil para brom-toluidine.

At first the toluidine passed over at 250°; but soon broke down in the distilling flask, throwing off red fumes; and a distillate solidified in the condenser tube which, when boiled up with animal charcoal and filtered, came out of the filtrate on cooling in the form of light yellow, translucent, orthorhombic crystals, which contained bromine and nitrogen, and melted at 284°; but the quantity of these was not sufficient to permit of a determination of their composition.

Summary.

The diazo compounds obtained from the nitranilines, ortho, meta, and para, when decomposed by alcohol, yielded mono-nitro benzene as the main product of the reaction.

The diazo compounds from ortho- and meta amido-benzoic acids, decomposed by alcohol, yielded ethyl benzoate as the main product of the reaction.

Para diazo benzoic acid nitrate, decomposed by alcohol, yielded [illegible] benzoic acid as the main product of the reaction.

Para-brom meta diazo-toluene nitrate, when decomposed by alcohol, gave a 38% yield of an oil, volatile in steam, as the main product of the reaction. The oil proved to be a mixture.

Decomposed by water and in toluene, Each of the nitraniline-diazo compounds

broke down to a tarry mass, which refused to yield a crystallized compound.

Decomposed in toluene, ortho-diazo benzoic acid nitrate gave unsymmetrical meta nitro salicylic acid as the chief product; while from meta diazo-benzoic acid sulphate, no crystallized compound resulted.

Para-diazo benzoic acid nitrate in toluene, gave [illegible] nitro para oxybenzoic acid, as the principal product of decomposition. Decomposed by water, this diazo yielded isomeric nitro para oxybenzoic acid as the main decomposition product; and a small quantity of para oxybenzoic acid as a secondary product.

All the decompositions by alcohol yielded aldehyde; and those by water, and in toluene all gave off nitrogen.

Conclusions.

The results obtained by the work [illegible] hitherto suggested concerning the conditions [illegible] [illegible]-reactions of diazo compounds with alcohol. All these decompositions studied by me, which yielded definite products, followed, with one exception, what has been termed by Remsen and Orndorff[1] the "Griess," or hydrogen, reaction; and the one decomposition which gave an ethoxy compound, viz, para diazo benzoic acid nitrate, had the diazo group in para position to the acid group.

Reviewing the efforts hitherto made looking toward the finding of the laws controlling these reactions, the eye of the investigator seems not to have been turned in the directions of what might be termed [illegible] influences [illegible]

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[1] Am. Chem. Journal. 9. 397

toward the influence exerted by the position relation of the diazo group to some other group in the compound. A study of my own work and of that done by others has convinced me that the law must be sought in an entirely different direction; and that the nature of the reaction depends, primarily, not at all upon position influence, but only on what [illegible] the abnormal influence of [illegible] i.e. upon the normal influence exerted by one or both the groups present in the compound; meaning by normal influence that influence exerted by the groups when, being unaccompanied by an exciting diazo group, decomposition takes place under normal conditions.

The [illegible]

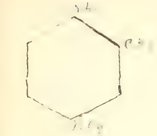
reactions of the three isomeric diazo nitro benzenes attracted my attention, and led me to a careful examination of the records of the decompositions of all diazo compounds

in connection with the nitro group [illegible]

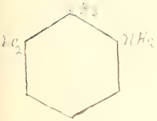
[illegible]

I made in all, the [illegible] sixty-two [illegible] decompositions. Of these, fifty-nine gave the hydrogen reaction; and of the three exceptions, two were not ordinary decompositions by alcohol, but by alcohol and sodium, and the compounds were subjected to the reducing influence exerted by the sodium and [illegible] under abnormal conditions, which I shall mention further; and the third, as will be seen, gave a very weak hydrogen reaction.

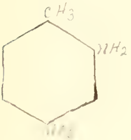
So numerous are the compounds known to give the hydrogen reaction that I shall mention only those that occur in relations which are known by experiment [illegible], when so influenced, to produce the [illegible] reaction. For the [illegible] [illegible], only the formulas of the compounds, and [illegible] will be given.



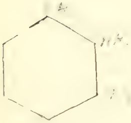
Beilstein & Kuhlberg. A. 158. 341



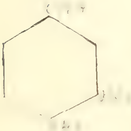
Cunerth. A. 172. 223.



Nölting & Collin. B. 17. 265, 268.



Lellmann & Würthner. A. 228. 240.

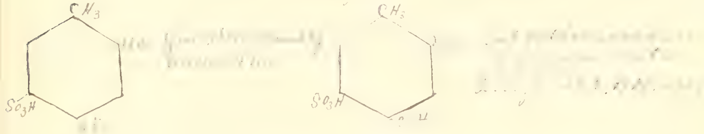


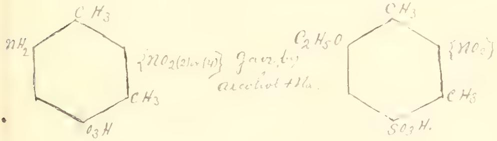
[illegible]

In all other cases, the nitro [illegible] [illegible] in company with another group or other groups which [illegible] in the [illegible] relation favors the [illegible] [illegible]

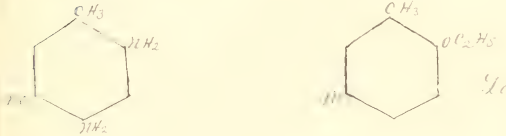
-pendent group influence exerted by the sulfo group.

The three exceptions recorded here are:


CH_3
SO_3H
CH_3
SO_3H


CH_3
NH_2
$\{NO_2(2 or (4)\}$
CH_3
O_3H
gave, by alcohol + Na.
CH_3
C_2H_5O
$\{NO_2\}$
CH_3
SO_3H.

Limpricht B. 18. 2190.


CH_3
NH_2
NH_2
CH_3
OC_2H_5

Ladenburg B. 8. 12

Referring to the last reaction, Remsen and Orndorff[1] remark that "the diazo group in the para position relatively to the methyl is replaced by hydrogen, while the other, which is in the ortho position relatively to methyl, is replaced by an ethoxy group." But may we not account for the double reaction as satisfactorily by supposing that the normal influence of the ortho methyl upon the

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[1] Am. Chem. Journal. 9. 398.

diazo group which, as we said, [illegible] that it, is sufficiently long to enable us to study the influence of [illegible] shift of the opening influence of the more simple nitro group? The influence of the para nitro group and of the nitro [illegible] there is [illegible] to condition the hydrogen more than in the case of the other diazo group.

It is worthy of notice, further, that in the [illegible] explained, the nitro group is para to the diazo; while in the second, one of the nitro groups is para to the diazo; yet in both cases the same change of mechanism ensues.

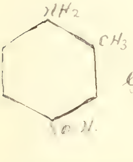
The results obtained by the study of the reactions of nitro compounds led us to examine the records concerning the influence of other groups. Besides the nitro group, the other groups which in the [illegible] compounds [illegible] [illegible] the halogens (Cl, Br, I): Meldola and [illegible]. [illegible]

are affected in the following groups, by the reagents to eliminate the chlorine, bromine or iodine; as this was not considered necessary.

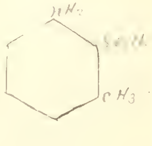
[illegible]

I found the records in nearly every one [illegible] [illegible] studied. Of these, [illegible] gave the hydrogen reaction. Of the eight exceptions, six were found to have been determined under pressure, 300 atm. or ammonia, and one by alcoholic chloride of sodium.

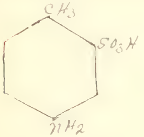
I should, besides these exceptions, mention a few more cases where [illegible] the SO_3H group added in the presence of nitrogenous or amines, or other means, tended to produce the ethoxy reaction as has been shown by experiment. Of these there are but two:-



Gerver A. 169.384 & Lorenz A. 172.181.

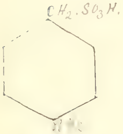


Those giving the Ethoxy reaction, in addition to the two already mentioned as exceptions in the case of the nitro compounds, are:


CH_3
SO_3H
NH_2

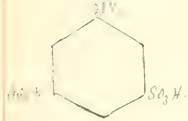
under pressure gave Ethoxy: at ordinary pressure, Griess

[illegible]



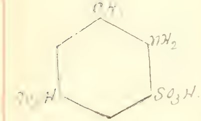
under 360 m.m. pressure.

Mohr, A. 221.222.



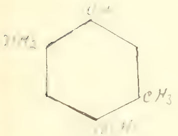
[illegible]

Zander. A. 198, 25.


CH_3
NH_2
SO_3H
$SO_3H.$

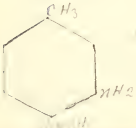
under 400 m.m. pressure.

Limpricht. B 18, 2176.



[illegible]

Limpricht, B. 18, 2189.



[illegible]

Haydruck. A. 172. 215. Payson A. 221. 215.

The first of these so-called exceptions is that [illegible] exceptions [illegible] explained [illegible] it occurs in hydrogen reaction; and this seems to furnish an answer to the question [illegible] [illegible] the common [illegible] [illegible] [illegible] e.g. the [illegible] decomposed under abnormal conditions, either under pressure or by addition of [illegible]. Such conditions seem to exist and [illegible] clearly favorable to the ethoxy reaction in the case [illegible] compounds containing the SO_3H group; and so perhaps in the [illegible] that [illegible] frequently [illegible] affect the hydrogen reaction of the [illegible].

Possibly a [illegible] decompositions under abnormal conditions of many compounds, which under normal conditions give the hydrogen reaction, would discover a decided tendency on the part of the abnormal conditions [illegible]

Supposing the [illegible] to have caused the ethoxy reaction in both of the cases

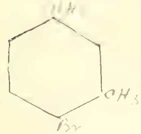
[illegible] exception to the normal rule [illegible] that [illegible], there is yet [illegible] [illegible] to the [illegible] [illegible] regarded by the [illegible].

There remains, however, one compound, the Cane sugar, [illegible] [illegible] [illegible] in its decomposition which escaped notice; [illegible] the exception, [illegible] reaction.

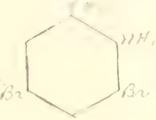
[illegible] [illegible], [illegible] of this [illegible] [illegible] [illegible] diagonis [illegible], the [illegible] [illegible] according to the [illegible] reaction.

There are six such compounds under consideration, two containing a [illegible], and one containing [illegible] which reaction [illegible].

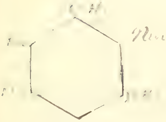
[illegible] Compounds containing [illegible] were found the diazo [illegible] of which have been recorded. In every case, there [illegible] structure, [illegible] [illegible] the compound [illegible] [illegible] [illegible] such directing influence is present [illegible]



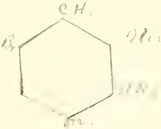
Wroblewsky A. 168. 173



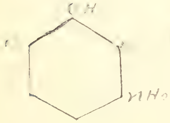
Wroblewsky A. 168. 179



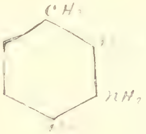
Nevile & Winther B. 13. 966


CH3
Br
NH2
Br

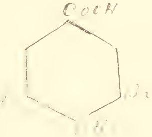
Nevile & Winther B. 13. 971



[illegible]



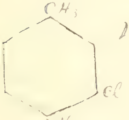
[illegible]



Beilstein & Geitner A. 139. 4.

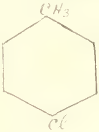
Turning to Chlorine compounds, we find [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] position that the [illegible] [illegible] [illegible] [illegible] [illegible] in addition to Chlorine, [illegible] [illegible]. In [illegible] Cases, the [illegible] reaction [illegible] on decomposition [illegible] [illegible], the reactions are not [illegible] would be [illegible] [illegible] of the Compound were accompanied by Chlorine, as [illegible] by Remsen & Orndorff[1] in their work on [illegible].

The Chlor [illegible] alluded to are

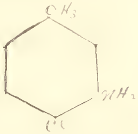


Wroblewsky B. 17. 2704 [illegible]

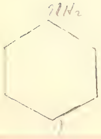
Hydrogen reaction



Ethoxy reaction



Ethoxy reaction



I is the only compound of iodine whose diazo decomposition has been studied } Rudolph B. 11. 81. and it gave the hydrogen reaction

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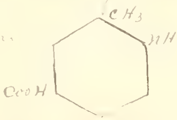
[1] Am. Chem. Journ. 9. 394.

The methyl group, whenever it exists in a single nucleus compound accompanied only by the diazo group or by a group whose influence it dominates, gives the reactions suggested by Remsen & Orndorff in their study of the three diazo toluenes; viz. para methyl favors the hydrogen reaction whereas the ortho and meta methyl favor the ethoxy reaction. But apparently the influence of this group is weak; in all the examples previously cited [illegible] that its influence is dominated by that of the nitro group, of the sulphonic acid group and of bromine.

On the other hand, all the cases hitherto studied tend to show that the influence of methyl dominates that of chlorine; and it was to be found to do the same in the case of iodine and of carboxyl.

Remsen & Orndorff's suggestion that the obtaining of the ethoxy reaction by decomposition of the diazo from 

appeared[1] to show that the influence of methyl

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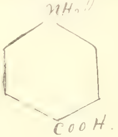
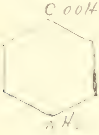
[1] Am. Chem. Jour. 9. 387

is stronger than that of carboxyl", is negatived by the result obtained by me[1] in the decomposition of the diazo compound from the homologous acid,

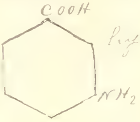


which gave the same reaction, although no methyl is present.

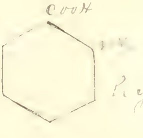
There are on record nine cases of decompositions of diazo compounds containing a [illegible] three described in this thesis[2] viz:



Ethoxy reaction.



hydrogen reaction.



hydrogen reaction.

Of the six remaining, four have the carboxyl group accompanied by influences which agree with the usual influence of this group, while in the other two, evidently that influence is dominated by that of other groups present.

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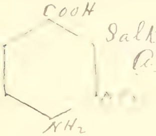
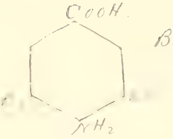
[1] This thesis.

These two cases are:—



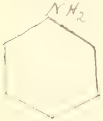
Salkowski.
A. 173.63.



Beilstein & Geitner.
A. 139.4

In each case the para carboxyl would, if left to itself, tend to produce the *Ethoxy* reaction, as is seen in the case of the diazo from para-amido benzoic acid. There is no evidence on record to show that the influence of this group is sufficiently strong to dominate that of an other group. Further reactions must be studied in order to fix its proper place in the scale of influence.

The *simplest possible* diazo compound, viz. that from



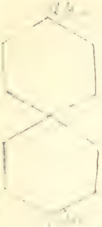
gives the *Ethoxy* reaction:

[illegible]

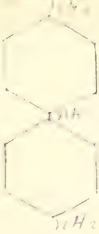
Eleven diazo compounds were found, having

[illegible]

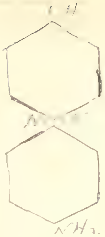
gave the *hydrogen* reaction. They are:—



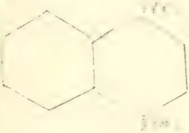
[illegible]



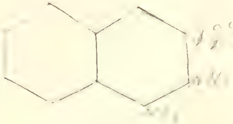
Nietzki u. Witt
B. 12. [illegible]



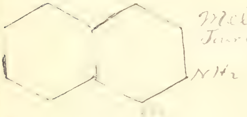
Schultz
B. 17. [illegible]



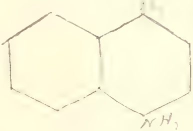
Beilstein u. Kuhlberg.
A. [illegible]



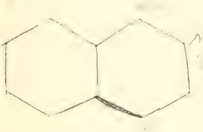
Jacobsen
[illegible]



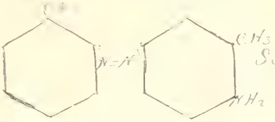
Meldola
Jour. Chem. Soc.
[illegible]



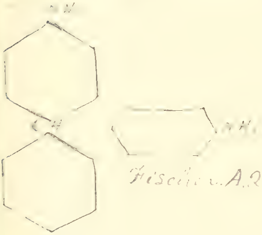
Rother
B. [illegible]



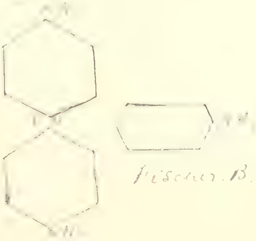
Liebermann.
A. 183. 260.


CH3
N=N
CH3
NH2

Schultz
B. 17. 477.



Fischer u. A. 206. 147.


NH2
CH
NH2
NH2

Fischer. B. 9. 899.

From the foregoing summary, I feel justified in drawing the following conclusions concerning dominating group influence in diazo-decompositions by alcohol:

1. The presence of the nitro group, in diazo-compounds [illegible] under normal conditions, occasions the hydrogen reaction, it matters not what other group, or groups, may be present [illegible].

2. The presence of the sulphonic acid group, in diazo-decompositions taking place under normal conditions, favors the hydrogen reaction; while abnormal conditions of decomposition, in presence of this group, favor the ethoxy reaction.

3. The presence of bromine, in diazo-decompositions, conditions the hydrogen reaction, it matters not what other group, or groups, may be present.

4. The presence of methyl in a diazo-compound, having a single-benzene-ring nucleus,

occasions the hydrogen reaction in the case of para nitro, and the ethoxy reaction in the case of [illegible] is alone, or accompanied only by Chlorine.

5. The normal influence of Chlorine, and of [illegible] the case of Chlorine seems to be a weak one, and is [illegible] basis on which to found a conclusion.

6. The normal influence of the Carboxyl Group, when present in a diazo compound, is to condition the hydrogen reaction in the cases of ortho and of meta carboxyls, and of the ethoxy reaction in the case of para carboxyl. This influence, however, is weak, and is dominated by that of the nitro group, of the sulphonic acid group, and, probably, also by that of other groups.

7. The Simplest diazo compound, having [illegible] decompose according to the ethoxy reaction.

8. All diazo compounds having more than one benzene ring as a nucleus decompose according to the hydrogen reaction.

I would suggest the following general theory of dominating group influence in diazo decomposition by alcohol when this takes place under normal conditions:—

In any diazo com[illegible]posed of one or more groups beside the diazo group joined to a single-benzene nucleus, [illegible] one of these groups [illegible] dominates that of all other groups present; and conditions that decomposition reaction which [illegible] in the compound;— i.e. the normal decomposition reaction of that group.

A series of investigations upon the decomposition reactions of a list of diazo compounds carefully selected with a view to the bearing of these reactions upon the solution of this question along the lines here suggested would speedily test the value of the theory herein advanced. The fact, that of the ninety-four [illegible] have been studied, all but one decomposed in accordance with the [illegible] suggested, cannot fail to lead to the conclusion that the theory of dominating group influence in diazo decomposition reactions is worthy of careful attention on the part of those searching for the laws controlling these reactions.

Before concluding this thesis I take the opportunity to express to Professor Ira Remsen my thanks for the friendly interest he has shown in my work. Without his helpful suggestions and the inspiration drawn from his instructions, the task undertaken would have proved a burdensome one. [illegible] [illegible] tion, to his influence is due the credit thereof.

[illegible] benefit derived from the instructions [illegible] training for original work; and it gives me pleasure here to acknowledge my obligations.

John Hopkins Stone